



Swiss Science Concentrates

A CHIMIA Column

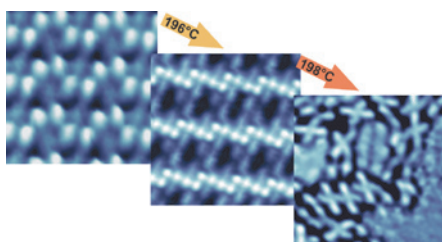
Short Abstracts of Interesting Recent Publications of Swiss Origin

Protecting-Group-Controlled Surface Chemistry-Organization and Heat-Induced Coupling of 4,4'-Di(*tert*-butoxycarbonylamino)biphenyl on Metal Surfaces

S. Boz, M. Stöhr,* U. Soydaner, and M. Mayor*, *Angew. Chem., Int. Ed.* **2009**, *48*, 3179

University of Basel and Forschungszentrum Karlsruhe GmbH

In this article the authors described a new strategy for the creation of surface-confined polymeric structures. It is based on a supramolecular self-assembly of pre-organized monomers and on a subsequent thermal activation to release protecting groups. The validity of this strategy was demonstrated using doubly Boc-protected diaminobiphenyl which was found to self-assemble on a Cu(111) surface. Depending on the temperature, this compound rearranges to form different polymeric structures. This concept offers many perspectives as both the molecular core and the protecting group can be easily modified to tune the properties of the obtained surfaces-immobilized polymers.

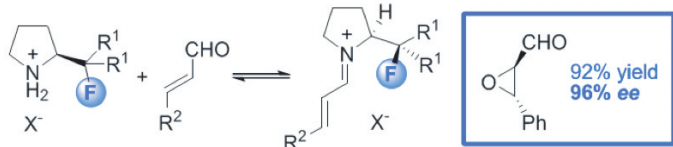


The Fluorine-Iminium Ion *Gauche* Effect: Proof of Principle and Application to Asymmetric Organocatalysis

C. Sparr, W. B. Schweizer, H. M. Senn, and R. Gilmour*, *Angew. Chem., Int. Ed.* **2009**, *48*, 3065

ETH Zürich and University of Glasgow

The propensity of highly electronegative elements, such as fluorine, to lower the energy of molecular orbitals to which they contribute has been widely exploited in the design of high-performance materials. In this article, fluorine is used to induce a *gauche* effect upon reversible formation of an iminium ion that provides a powerful method for the preorganization of transient intermediates that are central to secondary amine catalyzed processes. This phenomenon has been exploited in the design of a novel organocatalyst and is showcased in the stereoselective epoxidation of α,β -unsaturated aldehydes.

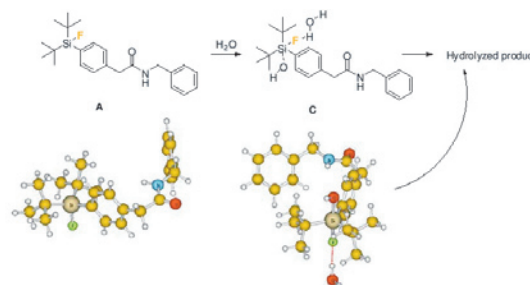


Organofluorosilanes as Model Compounds for ^{18}F -Labeled Silicon-Based PET Tracers and their Hydrolytic Stability: Experimental Data and Theoretical Calculations (PET = Positron Emission Tomography)

A. Höhne, L. Yu, L. Mu, M. Reiher,* U. Voigtmann, U. Klar, K. Graham, P. A. Schubiger, and S. M. Ametamey*, *Chem. Eur. J.* **2009**, *15*, 3736

ETH Zürich and Bayer Schering Pharma AG Berlin

Recently, it has been shown that silicon chemistry is a tool for the introduction of ^{18}F for positron emission tomography (PET) imaging into biomolecules. ^{18}F -labeled PET tracers must be however stable towards defluorination under physiological conditions. Here, a theoretical model of organofluorosilane hydrolysis is developed by means of density functional theory (DFT) methods that correlates with the experimentally determined hydrolytic half-lives and allows estimation of the stability of newly designed compounds (see Scheme).

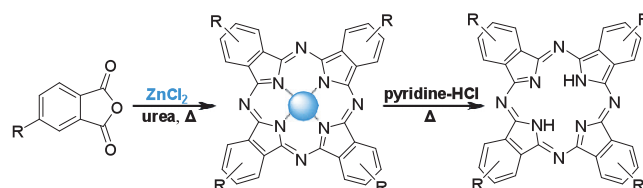


An Efficient Two-Step Synthesis of Metal-Free Phthalocyanines Using a Zn(II) Template

J. Alzeer, P. J. C. Roth, and N. W. Luedtke*, *Chem. Commun.* **2009**, 1970

University of Zurich

In this article, the authors described an efficient two-step synthesis of a new family of cationic phthalocyanines containing four guanidinium groups. Under the reaction conditions (pyridine-HCl, 120 °C) zinc was removed from both starting materials and products to provide the first published examples of Zn(II) removal without destroying the phthalocyanine itself. This demetallation reaction worked for electron-rich, electron-poor, alkyl-, ether-, and even unsubstituted zinc phthalocyanines. Since Zn(II) acts as a template to greatly enhance the yields of cyclotetramerization, this new demetallation reaction provides a high-yielding route to diverse, metal-free phthalocyanines.



Prepared by M. Austeri, R. Bach, J. Guin, A. Sharma, F. Toricelli, W. Zeghida, J. Lacour

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